

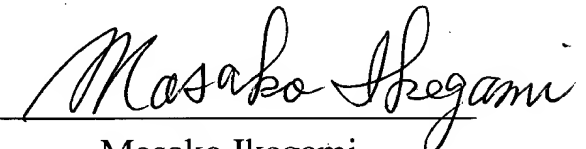


## DECLARATION

I, Masako Ikegami, of SHIGA INTERNATIONAL PATENT OFFICE, 2-3-1, Yaesu, Chuo-ku, Tokyo 104-8453 Japan, understand both English and Japanese, am the translator of the English document attached, and do hereby declare and state that the attached English document contains an accurate translation of Japanese Patent Application, First Publication No. 2000-294108 and that all statements made herein are true to the best of my knowledge.

Declared in Tokyo, Japan

This 23th day of February, 2004

  
Masako Ikegami



[Document Type] Specification

[Title of the Invention] ENERGY-RAY CURABLE COLORED  
COMPOSITION FOR INK JET RECORDING AND COLOR FILTER

[Claims]

[Claim 1] An energy-ray curable colored composition for ink jet recording, comprising (a) a coloring material and (b) an amino resin having a carboxyl group and/or a phenolic hydroxyl group.

[Claim 2] The energy-ray curable colored composition for ink jet recording according to claim 1, wherein the amino resin (b) is an amino resin obtained by condensing (4,6-diamino-1,3,5-triazin-2-yl)benzoic acid with at least one aldehyde compound selected from the group consisting of formaldehyde, glyoxylic acid, succinsemialdehyde, and hydroxybenzaldehyde.

[Claim 3] The energy-ray curable colored composition for ink jet recording according to claim 1, wherein the amino resin (b) is an amino resin obtained by condensing at least one triazine compound selected from the group consisting of melamine, benzoguanamine, and (4,6-diamino-1,3,5-triazin-2-yl)benzoic acid with at least one aldehyde compound selected from the group consisting of glyoxylic acid, succinsemialdehyde, and hydroxybenzaldehyde.

[Claim 4] The energy-ray curable colored composition for ink jet recording according any one of claims 1 to 3,

wherein the energy ray is heat ray.

[Claim 5] The energy-ray curable colored composition for ink jet recording according any one of claims 1 to 3, wherein the energy ray is light having a wavelength in the range of 200 to 500 nm.

[Claim 6] A color filter obtained by using the energy-ray curable colored composition for ink jet recording according any one of claims 1 to 5.

[Detailed Description of the Invention]

[0001]

[Technical Filed of the Invention]

The present invention relates to an energy-ray curable colored composition and to a color filter using the same. More particularly, the present invention relates to an energy-ray curable colored composition suited for uses which require durability after passing through the step of forming a pattern by means of an ink-jet printing method, for example, coating compositions, printing inks, colored display panels using the compositions or the inks, materials comprising a substrate wherein a colored image is formed on the substrate such as color proof, especially color filters used in color liquid crystal displays, color scanners, and solid image pick-up elements, and to a color filter using the same.

[0002]

[Prior Art]

Examples of energy-ray curable colored compositions using coloring materials such as pigments and dyes known to date are (i) photocurable colored compositions obtained by adding a photopolymerizable monomer and a photopolymerization initiator to a colored composition in which a coloring material is dispersed or dissolved in a binder resin solution and (ii) thermosetting colored compositions obtained by dispersing or dissolving a coloring material in a thermosetting resin. There has also been known a method of forming a colored image by a method of coating the colored composition on a substrate using an ink-jet printing method to form colored patterns and exposing the coated substrate to light or heat energy, thereby to fix the colored patterns. Examples of available application of these energy-ray curable colored compositions include color filters used in color liquid crystal displays, color scanners, solid image pick-up elements and the like.

[0003]

The color filter is formed by arranging coloring materials on each pixel to selectively transmit three primary colors of light (e.g. red, green, and blue) or to selectively reflect three primary colors (e.g. cyan, magenta, and yellow), on a transparent substrate provided with a shade film called as a black matrix.

As the method of forming the color filter, a

photolithography method, an electrodeposition method, a printing method, and an ink-jet printing method are known and the photolithography method is mainly used at present. This method is a method comprising many steps, wherein the three steps of applying a photocurable composition to a substrate, exposing the substrate to radiation energy through a pattern-mask, and dissolving the unnecessary portion and washing are repeated for each red, green, and blue pixels or each cyan, magenta, and yellow pixels, thereby to form a color filter. On the other hand, the ink-jet printing method, which can form red, green, and blue, or cyan, magenta, and yellow pixels in one step, has received much attention because of its low cost due to the small number of steps.

[0004]

Although methods of forming a color filter by the ink-jet printing method are disclosed in Japanese Unexamined Patent Application, First Publication No. Sho 59-75205, Japanese Unexamined Patent Application, First Publication No. Sho 61-245106, and Japanese Unexamined Patent Application, First Publication No. Sho 63-294503, the color filters obtained by these methods are inferior in heat resistance and chemical resistance because the coloring material is a dye type material.

On the other hand, various methods using a resin and a pigment have been proposed as methods for producing colored

layers having excellent heat resistance and chemical resistance. For example, Japanese Unexamined Patent Application, First Publication No. Hei 5-224007 discloses a color filter using ink-jet printing ink comprising a melamine resin and a colorant; Japanese Unexamined Patent Application, First Publication No. Hei 8-171010 discloses a color filter using thermosetting or photocurable ink-jet printing ink containing an acrylamide based polymer; Japanese Unexamined Patent Application, First Publication No. Hei 10-17813 discloses a color filter using ink-jet printing ink consisting mainly of a melamine resin, a polycarboxylic acid derivative, and an amine type stabilizer; and Japanese Unexamined Patent Application, First Publication No. Hei 7-188596 discloses ink for thermosetting ink-jet recording using a thermosetting resin and a specific amine as a dispersant.

[0005]

With the recent increase in the size of liquid crystal displays (abbreviated as LCDs), many requirements have arisen for the materials for color filters in the process of manufacturing color LCDs, and examples thereof include heat resistance which is required in the deposition or sputtering processes of a transparent electrode such as ITO and baking process of a color filter, and solvent resistance, which is required in the cleaning process and coating process for

oriented film. Another requirement is light resistance since the image information is formed by light which is transmitted through the color filter during displaying the image.

[0006]

Ink-jet printing ink containing an acrylic resin has had the drawback that the resin is liable to decompose when the temperature exceeds 200°C. Although Japanese Unexamined Patent Application, First Publication No. Hei 5-224007 proposes ink-jet printing ink using a thermosetting resin such as a melamine resin for the purpose of improving the heat resistance, this method has the following drawbacks. Since an organic or inorganic acid or an amine or ammonium salt thereof is used as a curing accelerator in combination in the ink used in the method, these compounds remain as impurities in the film, thereby contaminating the sputtering apparatus upon formation of ITO transparent electrodes or such an ink has a short pot life when it is made as an ink in one package type.

[0007]

It has been required to develop an energy-ray curable colored composition, which has excellent heat resistance and does not undergo color changes due to heat, resulting from the increase of the temperature during the deposition of transparent electrodes by vacuum deposition or sputtering process or baking process. In view of the above, it is

required to develop an energy-ray curable colored composition for ink jet recording, which exhibits excellent physical properties of coating layer such as heat resistance and chemical resistance and is free from impurities that can cause deterioration of performances of the color filter and the liquid crystal.

[0008]

[Problems to be solved by the Invention]

An object of the present invention is to provide an energy-ray curable colored composition for ink jet recording suited for practical use, which is superior in storage stability and can form a coating layer having excellent heat resistance and solvent resistance or chemical resistance, especially heat resistance by means of an ink-jet printing method, and a color filter using the same.

[Means for Solving the Problems]

[0009]

To attain the object described above, the present inventors have intensively studied and found that an energy-ray curable colored composition for ink jet recording, which is superior in storage stability and can form a coating layer having excellent heat resistance, and a color filter, which is excellent in transparency of a coloring material and color purity, can be obtained by using an amino resin having a carboxyl group and/or a phenol hydroxyl group as a binder



resin in an energy-ray curable colored composition for ink jet recording, containing a coloring material and a binder resin, and a color filter using the same. Thus, the present invention has been completed.

[0010]

The present invention includes:

(1) An energy-ray curable colored composition for ink jet recording, comprising (a) a coloring material and (b) an amino resin having a carboxyl group and/or a phenol hydroxyl group;

[0011]

(2) the energy-ray curable colored composition for ink jet recording according to (1), wherein the amino resin (b) is an amino resin obtained by condensing (4,6-diamino-1,3,5-triazin-2-yl)benzoic acid with at least one aldehyde compound selected from the group consisting of formaldehyde, glyoxylic acid, succinsemialdehyde, and hydroxybenzaldehyde;

[0012]

(3) the energy-ray curable colored composition for ink jet recording according to (1), wherein the amino resin (b) is an amino resin obtained by condensing at least one triazine compound selected from the group consisting of melamine, benzoguanamine, and (4,6-diamino-1,3,5-triazin-2-yl)benzoic acid with at least one aldehyde compound selected from the group consisting of glyoxylic acid, succinsemialdehyde, and

hydroxybenzaldehyde;

[0013]

(4) the energy-ray curable colored composition for ink jet recording according any one of (1) to (3), wherein the energy ray is heat ray;

[0014]

(5) the energy-ray curable colored composition for ink jet recording according any one of (1) to (3), wherein the energy ray is light having a wavelength in the range of 200 to 500 nm; and

[0015]

(6) a color filter obtained by using the energy-ray curable colored composition for ink jet recording according to any one of (1) to (5).

[0016]

#### [Embodiments of the Invention]

The present invention will now be described in more detail.

The present invention is directed to an energy-ray curable colored composition comprising a coloring material and a binder resin for ink jet recording, wherein the binder resin is (b) an amino resin having a carboxyl group and/or a phenolic hydroxyl group.

[0017]

Generally, the amino resin can be obtained by

condensing an amino compound such as urea, melamine, benzoguanamine, acetoguanamine, or guanamine based compound with an aldehyde compound such as formaldehyde, paraformaldehyde, or acetaldehyde. It can also be obtained by etherifying the condensation product using an alcohol for etherification.

[0018]

Examples of the amino compound used in the present invention include, but are not limited to, urea, melamine, benzoguanamine, acetoguanamine, cyclohexanecarboguanamine, phthaloguanamine, steroguanamine, spiroguanamine, 2-, 3- or 4-(4,6-diamino-1,3,5-triazin-2-yl)benzoic acid, and 2-, 3- or 4-(4,6-diamino-1,3,5-triazin-2-yl)-phenol. Among these amino compounds, melamine, benzoguanamine, or (4,6-diamino-1,3,5-triazin-2-yl)benzoic acid is particularly preferable in view of storage stability and heat resistance.

[0019]

Examples of the aldehyde compound used in the present invention include, but are not limited to, formaldehyde, paraformaldehyde, acetaldehyde, propionaldehyde, butylaldehyde, glyoxazol, glyoxalic acid, succinsemialdehyde, 2-, 3-, or 4-hydroxybenzaldehyde; formaldehyde condensates such as trioxane or paraformaldehyde; aqueous solutions such as an aqueous formaldehyde solution; and methylhemiformal, n-butylhemiformal or isobutylhemiformal. Among these aldehyde

compounds, formaldehyde, glyoxylic acid, succinsemialdehyde, or 4-hydroxybenzaldehyde is particularly preferable in view of heat resistance. These aldehyde compounds may be used alone or in combination, as a matter of course.

[0020]

The present invention is characterized in that the amino resin has a carboxyl group and/or a phenolic hydroxyl group, and therefore when an amino compound for amino resin, as the raw material, which has neither a carboxyl group nor a phenolic hydroxyl group, is urea, melamine, benoguanamine, acetoguanamine, cyclohexanecarboguanamine, phthaloguanamine, steroguanamine, or spiroguanamine, it is indispensable that an aldehyde compound to be used have at least a carboxyl group or a phenolic hydroxyl group. In this case, the aldehyde compound is preferably glyoxylic acid, succinsemialdehyde, or 2-, 3-, or 4-hydroxybenzaldehyde.

[0021]

When the amino compound for amino resin, as the raw material, has a carboxyl group and a phenolic hydroxyl group, such as 2-, 3- or 4-(4,6-diamino-1,3,5-triazin-2-yl)benzoic acid, and 2-, 3- or 4-(4,6-diamino-1,3,5-triazin-2-yl)-phenol, the aldehyde compound to be used is not specifically limited and the above-described compounds can be used.

[0022]

As the amino resin in the present invention, not only

those obtained by condensing one amino compound with one aldehyde compound, but also those obtained by condensing one or more kinds of amino compounds with one or more kinds of aldehyde compounds can be used. In this case, at least one of the amino compound and aldehyde compound may have at least one carboxyl group and phenolic hydroxyl group. For example, benzoguanamine and 4-(4,6-diamino-1,3,5-triazin-2-yl)benzoic acid can be mixed in a desired proportion and the resulting mixture can be condensed with formaldehyde or a mixture of formaldehyde and a glyoxylic acid in a desired proportion. An acid value of the resulting amino resin can be adjusted by using plural kinds of amino compounds and/or aldehyde compounds as the raw material, thereby making it control the solubility of the energy-ray curable colored composition in the solvent.

[0023]

The alcohol for etherification used in the present invention is useful to stabilize a product of the condensation reaction of the amino compound, as the raw material, and the aldehyde compound. Examples of the alcohol include, but are not limited to, various alcohols having 1 to 8 carbon atoms, such as methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, sec-butanol, tert-butanol, cyclohexanol, n-pentanol, isopentanol, methylisobutylcarbinol, benzyl alcohol, furfuryl alcohol, n-octanol, sec-octanol, 2-

ethylhexyl alcohol, and allyl alcohol;

[0024]

various ether alcohols such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, ethylene glycol monoisobutyl ether, ethylene glycol mono-tert-butyl ether, ethylene glycol mono-iso-propyl ether, ethylene glycol monohexyl ether, 3-methoxybutanol, 3-methyl-3-methoxybutanol, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, propylene glycol monomethyl ether, and dipropylene glycol monomethyl ether; and

[0025]

various ketone alcohols such as ketobutanol, diacetone alcohol, and acetoin. These alcohols may be used alone or in combination, as a matter of course. Among these alcohols, methanol, ethanol, n-propnaol, isopropanol, n-butanol, and isobutanol are particularly preferable in view of reactivity, cost and crosslinkability of the resulting amino resin.

[0026]

The amino resin (b) used in the present invention can be prepared by the method of reacting 1.0 mol of the amino compound, 1.5 to 8 mol of the aldehyde compound, and 3 to 20 mol of the alcohol for etherification, according to the method described in Japanese Unexamined Patent Application, First Publication No. Hei 9-143169, Japanese Unexamined

Patent Application, First Publication No. Hei 8-176249, Japanese Unexamined Patent Application, First Publication No. Hei 9-208821 or Japanese Unexamined Patent Application, First Publication No. Hei 10-140015. In this case, a conventionally known solvent can be used.

[0027]

When using two or more amino compounds and/or aldehyde compounds, as the raw material for amino resin, in combination, the proportion is not specifically limited. When the acid value is too small, the solubility in a water-soluble solvent is poor and the curing action due to the carboxyl group or phenolic hydroxyl group on thermosetting tends to be lowered. On the other hand, when the acid value is too large, the water resistance after curing tends to become poor. Accordingly, the composition is preferably adjusted so that the acid value of the amino resin is within a range from 20 to 250 mg KOH/g.

[0028]

The amino resin (b) can be prepared by conventionally known methods. Examples thereof include:

(1) a method of adding an amino compound to a solution prepared by adding an aldehyde compound to an alcohol for etherification, and reacting the mixed solution at a temperature of 50 to 140°C for 20 minutes to 7 hours, if necessary, in the presence of an acidic catalyst, thereby

simultaneously carrying out the condensation reaction and etherification reaction,

[0029]

(2) a method of methylolating at a pH within a range from 8 to 10 with a solution containing an aldehyde compound and an amino compound, and then carrying out the alkyl etherification reaction at a pH within a range from 2 to 6 in the presence of an alcohol for etherification,

[0030]

(3) a method of adding at least one amino compound selected from the group consisting of urea, melamine, benzoguanamine, acetoguanamine, cyclohexanecarboguanamine, phthaloguanamine, steroguanamine, and spiroguanamine to a solution prepared by adding an aldehyde compound to an alcohol for etherification, and adding (4,6-diamino-1,3,5-triazin-2-yl)benzoic acid and/or (4,6-diamino-1,3,5-triazin-2-yl)-phenol during the condensation reaction and etherification reaction, and

[0031]

(4) a method of adding at least one aldehyde compound selected from the group consisting of formaldehyde, paraformaldehyde, acetaldehyde, propionaldehyde, butylaldehyde, glyoxazol, glyoxylic acid, succinsemialdehyde, and 2-, 3- or 4-hydroxybenzaldehyde to an alcohol for etherification, and adding at least one amino compound selected from the group consisting of urea, melamine,



benzoguanamine, acetoguanamine, cyclohexanecarboguanamine, phthaloguanamine, steroguanamine, spiroguanamine, (4,6-diamino-1,3,5-triazin-2-yl)benzoic acid, and (4,6-diamino-1,3,5-triazin-2-yl)-phenol, thereby carrying out the condensation reaction and etherification reaction.

[0032]

It is also possible to dissolve or disperse in water or a mixture of water and a water-soluble solvent by completely or partially neutralizing the carboxyl group and/or phenolic hydroxyl group introduced into the amino resin (b) with various volatile bases such as ammonia and organic amine.

[0033]

Examples of the organic amine include, but are not limited to, alkylamines such as monomethylamine, dimethylamine, monoethylamine, diethylamine, and triethylamine; hydroxylamines such as N-methylaminoethanol, N,N-dimethylaminoethanol, N,N-diethylaminoethanol, 2-amino-2-methylpropanol, diethanolamine, and triethanolamine; and polyvalent amines such as ethylenediamine and diethylenetriamine. These organic amines may be used alone or in combination.

[0034]

The amino resin (b) in the present invention is used as a thermosetting binder resin and a polymer such as an acryl polymer can be allowed to coexist so as to further adjust the

solubility in the solvent. When using an aqueous solvent, the amino resin preferably has a carboxyl group.

As the polymer such as an acryl polymer, a conventionally known polymer can be used and a copolymerizable ethylenically unsaturated monomer can be used after being polymerized. As the ethylenically unsaturated monomer, a conventionally known ethylenically unsaturated monomer can be used.

[0035]

Specific examples of the ethylenically unsaturated monomer include (meth)acrylic acid esters (the term (meth)acryl as used herein means acryl or methacryl) such as methyl (meth)acrylate, ethyl (meth)acrylate, propyl (meth)acrylate, butyl (meth)acrylate, hexyl (meth)acrylate, octyl (meth)acrylate, decyl (meth)acrylate, dodecyl (meth)acrylate, tetradecyl (meth)acrylate, hexadecyl (meth)acrylate, stearyl (meth)acrylate, octadecyl (meth)acrylate, and docosyl (meth)acrylate;

[0036]

(meth)acrylic acid esters having an alicyclic alkyl group, such as cyclohexyl (meth)acrylate, isobornyl (meth)acrylate, dicyclopentanyl (meth)acrylate, and dicyclopentenylloxyethyl (meth)acrylate, (meth)acrylic acid ester of tetrahydrofurfuryl alcohol and  $\epsilon$ -caprolactone; (meth)acrylic acid esters having an aromatic ring, such as benzyloxyethyl

(meth)acrylate, benzyl (meth)acrylate, phenylethyl (meth)acrylate, phenoxyethyl (meth)acrylate, phenoxydiethylene glycol (meth)acrylate, and 2-hydroxy-3-phenoxypropyl (meth)acrylate;

[0037]

(meth)acrylic acid esters having a hydroxyalkyl group, such as hydroxyethyl (meth)acrylate, hydroxypropyl (meth)acrylate, and glycerol (meth)acrylate; (meth)acrylic acid esters having a polyalkylene glycol, such as hydroxyethyl lactone-modified (meth)acrylate, polyethylene glycol (meth)acrylate, and polypropylene glycol (meth)acrylate;

[0038]

glycidyl (meth)acrylate, glycidyl  $\alpha$ -ethyl (meth)acrylate, glycidyl  $\alpha$ -n-propyl (meth)acrylate, glycidyl  $\alpha$ -n-butyl (meth)acrylate, (meth)acrylic acid-3,4-epoxybutyl, (meth)acrylic acid-6,7-epoxypentyl, or  $\alpha$ -ethyl(meth)acrylic acid-6,7-epoxybutyl; alicyclic epoxy monomer such as (meth)acrylic acid-3,4-epoxycyclohexyl, lactone-modified (meth)acrylic acid-3,4-epoxycyclohexyl, or vinylcyclohexane oxide, and glycidyl group-containing ethylenically unsaturated monomer obtained by reacting a compound having two or more alicyclic epoxy groups in the molecule with a compound having a polymerizable unsaturated double bond and a group having reactivity with an alicyclic epoxy group in the molecule;

[0039]

unsaturated dicarboxylic acid esters such as dimethyl fumarate, diethyl fumarate, dibutyl fumarate, dimethyl itaconate, dibutyl itaconate, methylethyl fumarate, methylbutyl fumarate, and methylethyl itaconate; styrene derivatives such as styrene,  $\alpha$ -methylstyrene, and chlorostyrene; diene compounds such as butadiene, isoprene, piperylene, and dimethylbutadiene; vinyl halide and vinylidene halide, such as vinyl chloride and vinyl bromide;

[0040]

unsaturated ketones such as methyl vinyl ketone and butyl vinyl ketone; vinyl esters such as vinyl acetate and vinyl butyrate; vinyl ethers such as methyl vinyl ether and butyl vinyl ether; vinyl cyanides such as acrylonitrile, methacrylonitrile, and vinylidene cyanide; acrylamide and alkyd-substituted amide thereof, and N-substituted maleimides such as N-phenylmaleimide and N-cyclohexylmaleimide;

[0041]

fluorine-containing  $\alpha$ -olefins such as vinyl fluoride, vinylidene fluoride, trifluoroethylene, chlorotrifluoroethylene, bromotrifluoroethylene, pentafluoropropylene, or hexafluoropropylene; or (per)fluoroalkyl perfluorovinyl ethers wherein a (per)fluoroalkyl group has 1 to 18 carbon atoms, such as trifluoromethyl trifluorovinyl ether, pentafluoroethyl

trifluorovinyl ether, or heptafluoropropyl trifluorovinyl ether;

[0042]

fluorine-containing ethylenically unsaturated monomers, for example, (per)fluoroalkyl (meth)acrylates wherein a (per)fluoroalkyl group has 1 to 18 carbon atoms, such as 2,2,2-trifluoroethyl (meth)acrylate, 2,2,3,3-tetrafluoropropyl (meth)acrylate, 1H,1H,5H-octafluoropentyl (meth)acrylate, 1H,1H,2H,2H-heptafluorodecyl (meth)acrylate, or perfluoroethyloxyethyl (meth)acrylate;

[0043]

silyl group-containing (meth)acrylates such as  $\gamma$ -methacryloxypropyltrimethoxysilane; and N,N-dialkylaminoalkyl (meth)acrylates such as N,N-dimethylaminoethyl (meth)acrylate, N,N-diethylaminoethyl (meth)acrylate, or N,N-diethylaminopropyl (meth)acrylate. These ethylenically unsaturated monomers can be used alone or in combination, as a matter of course.

[0044]

A polymer having a carboxyl group, such as acryl is prepared by copolymerizing an ethylenically unsaturated monomer having a carboxyl group with the above ethylenically unsaturated monomer. Specific examples of the ethylenically unsaturated monomer having a carboxyl group include ethylenically unsaturated mono- and dicarboxylic acids such

as acrylic acid, methacrylic acid, coumalic acid, itaconic acid, maleic acid, or fumaric acid; and maleic acid monoalkyl ester, fumaric acid monoalkyl ester, or itaconic acid monoalkyl ester.

[0045]

The copolymer form of the ethylenically unsaturated monomer is not specifically limited and the copolymer may be any of random copolymer, block copolymer, graft copolymer and the like obtained by addition polymerization in the presence of a radical polymerization initiator. The copolymerization method thereof to be used may be a known polymerization method such as a bulk polymerization method, solution polymerization method, suspension polymerization method, or emulsion polymerization method.

[0046]

Examples of the radical polymerization initiator include azo compounds such as 2,2'-azobisisobutyronitrile, 2,2'-azobis-(2,4-dimethylvaleronitrile), and 2,2'-azobis-(4-methoxy-2,4-dimethylvaleronitrile), and organic peroxides and hydrogen peroxides, such as benzoyl peroxide, lauroyl peroxide, t-butyl peroxy-pivalate, 1,1'-bis-(t-butylperoxy)cyclohexane, t-amylperoxy-2-ethylhexanoate, and t-hexylperoxy-2-ethylhexanoate. When using the organic peroxide as the radical polymerization initiator in combination with a reducing agent, it serves as a redox type

initiator. In the preparation of these copolymers, conventionally known solvents can be used.

[0047]

In the case in which the aforementioned polymer such as an acryl polymer is used as a binder resin, together with an amino resin (b), and a proportion of the amino resin (b) in the binder resin is small, the resulting cured coating layer is inferior in heat resistance and changes in crystal form of the coloring material and crystal growth occur, thereby causing changes in brightness of color (transparency) and deterioration of chromaticity. Therefore, the proportion of the amino resin (b) in the entire binder resin is preferably 10% by weight or more, and particularly preferably 20% by weight or more.

[0048]

The energy-ray curable colored composition for ink jet recording of the present invention contains coloring materials (a) such as dyes or pigments, together with the above amino resin (b). As the coloring material, pigments are preferably used in view of heat resistance and light resistance.

[0049]

Dyes used in the present invention may include conventionally known dyes and those described in "Dye Handbook" (edited by Organic Synthetic Chemistry Association,

published in 1970; "Color Material Engineering Handbook" (edited by Japan Society of Color Material, published in 1989); "Technology and Market of Industrial Pigment" (edited by CMC, published in 1983); and "Chemical Handbook, Applied Chemistry Edition" (edited by The Chemical Society of Japan, published by Maruzen Co., Ltd. in 1986). Specific examples thereof include azo dyes, metal chain salt azo dyes, pyrazolone azo dyes, naphthoquinone dyes, anthraquinone dyes, phthalocyanine dyes, carbonium dyes, quinoneimine dyes, methine dyes, cyanine dyes, indigo dyes, quinoline dyes, nitro type dyes, xanthene type dyes, thiazine type dyes, azine dyes, oxazine dyes, and squalilium dyes.

[0050]

The pigments used in the present invention include commercially available pigments, and pigments described in the Color Index Handbook, "Latest Pigment Handbook" (edited by the Pigment Technology Association of Japan, published in 1977), "Latest Pigment Applied Technology" (CMC publications, published in 1986) and "Printing Ink Technology" (CMC publications, published in 1984).

[0051]

Specific examples of the pigments include inorganic pigments such as barium sulfate, lead sulfate, titanium oxide, yellow lead oxide, chrome oxide, red iron oxide, and carbon black; and organic pigments such as anthraquinone type



pigments, perylene type pigments, disazo pigments, phthalocyanine type pigments, isoindolinone type pigments, dioxazine type pigments, quinacridon pigments, perinone pigments, triphenylmethane type pigments, thioindigo pigments, and diketopyrrolopyrrole type pigments. These pigments can be used alone or in combination. Among these pigments, anthraquinone type pigments, diketopyrrolopyrrole type pigments, phthalocyanine type pigments, dioxazine type pigments and carbon black are particularly preferable.

[0052]

Specific examples of these pigments are indicated below by Color Index (C.I.) Number and, as a matter of course, they are not limited to the following compounds:

red pigments such as C.I. Pigment Red 9, C.I. Pigment Red 97, C.I. Pigment Red 122, C.I. Pigment Red 123, C.I. Pigment Red 149, C.I. Pigment Red 168, C.I. Pigment Red 177, C.I. Pigment Red 180, C.I. Pigment Red 192, C.I. Pigment Red 215, C.I. Pigment Red 216, C.I. Pigment Red 217, C.I. Pigment Red 220, C.I. Pigment Red 223, C.I. Pigment Red 224, C.I. Pigment Red 226, C.I. Pigment Red 227, C.I. Pigment Red 228, C.I. Pigment Red 240, C.I. Pigment Red 254, and C.I. Pigment Red 48:1;

[0053]

green pigments such as C.I. Pigment Green 7 and C.I. Pigment Green 36;

[0054]

blue pigments such as C.I. Pigment Blue 15, C.I. Pigment Blue 15:6, C.I. Pigment Blue 22, C.I. Pigment Blue 60, and C.I. Pigment Blue 64;

[0055]

violet pigments such as C.I. Pigment Violet 19, C.I. Pigment Violet 23, C.I. Pigment Violet 29, C.I. Pigment Violet 30, C.I. Pigment Violet 37, C.I. Pigment Violet 40, and C.I. Pigment Violet 50;

[0056]

yellow pigments such as C.I. Pigment Yellow 20, C.I. Pigment Yellow 24, C.I. Pigment Yellow 83, C.I. Pigment Yellow 86, C.I. Pigment Yellow 93, C.I. Pigment Yellow 109, C.I. Pigment Yellow 110, C.I. Pigment Yellow 117, C.I. Pigment Yellow 125, C.I. Pigment Yellow 137, C.I. Pigment Yellow 138, C.I. Pigment Yellow 139, C.I. Pigment Yellow 147, C.I. Pigment Yellow 148, C.I. Pigment Yellow 150, C.I. Pigment Yellow 153, C.I. Pigment Yellow 154, C.I. Pigment Yellow 166, C.I. Pigment Yellow 168, and C.I. Pigment Yellow 185; and

[0057]

black pigments such as C.I. Pigment Black 7.

These coloring materials (a) can be used alone or in combination.

[0058]

An energy-ray curable colored composition for ink jet recording, which contains a coloring material (a) dispersed

therein, is usually prepared by using at least the above coloring material (a) and the binder resin (b) in combination with a solvent. Examples of the solvent used in the preparation of the colored composition containing the coloring material dispersed therein include aromatic solvents such as toluene, xylene, and methoxybenzene; acetic acid ester solvents such as ethyl acetate, butyl acetate, propylene glycol monomethyl ether acetate, and propylene glycol monoethyl ether acetate; propionate solvents such as ethoxyethyl propionate; alcohol solvents such as methanol, ethanol, propanol, and ethylene glycol;

[0059]

ether solvents such as butylcellosolve, propylene glycol monomethyl ether, diethylene glycol ethyl ether, and diethylene glycol dimethyl ether; ketone solvents such as methyl ethyl ketone, methyl isobutyl ketone, and cyclohexanone; aliphatic hydrocarbon solvents such as hexane; nitrogen compound type solvents such as N,N-dimethylformamide,  $\gamma$ -butyrolactam, N-methyl-2-pyrrolidone, aniline, and pyridine; lactone solvents such as  $\gamma$ -butyrolactone; carbamic acid esters such as a mixture of methyl carbamate and ethyl carbamate in a mixing ratio of 48:52; and water. Since the amino resin used in the present invention is hydrophilic, the solvent used for the colored composition may be water or a solvent consisting mainly of water.

Among these solvents, those having a boiling point of 80 to 200°C are preferably selected. These solvents may be used alone or in combination.

[0060]

In the preparation of the colored composition containing the coloring material dispersed therein, a dispersant can be used in combination. The dispersant is not specifically limited and a conventionally known dispersant can be used. Specific examples thereof include surfactants, intermediates of pigments, intermediates of dyes, and resin type dispersants such as polyester compounds, polyamide compounds, and polyurethane compounds.

[0061]

Examples of commercially available products of this resin type dispersant include DISPERBYK 130, DISPERBYK 161, DISPERBYK 162, DISPERBYK 163, DISPERBYK 170, EFKA 46, EFKA 47, SOLSPERSE 32550, SOLSPERSE 24000, AJISPER PB811 and AJISPER PB814. Acrylic and polyethylenene resin type dispersants can also be used.

[0062]

The amount of the coloring material (a) is preferably within a range from 10 to 70% by weight based on the entire solid content in the energy-ray curable colored composition. When using the dispersant with the coloring material, the amount of the dispersant is preferably within a range from 5

to 50% by weight based on the coloring material (a).

[0063]

The average particle diameter of the pigment is preferably within a range from 0.005 to 3  $\mu\text{m}$ , and more preferably from 0.01 to 1  $\mu\text{m}$ . When the average particle diameter is smaller than the above range, thixotropy may occur and, therefore, good applicability cannot be obtained. On the other hand, when the average particle diameter is larger than the above range, the resulting coating layer has poor transparency. To obtain the average particle diameter within the above range, a dispersion treatment using a ball mill, sand mill, bead mill, three-roll mill, paint shaker, attriter, dispersion stirrer, ultrasonic wave and the like is effective.

[0064]

The energy-ray curable colored composition for ink jet recording of the present invention itself serves as a thermosetting resin when the energy ray is a heat ray. Since the amino resin in the present invention has a carboxyl group or a phenolic hydroxyl group, it has such an advantage in that a curing accelerator need not be used in combination and the resulting cured article does not contain impurities originating in the remaining curing accelerator.

[0065]

In the case of an energy ray having a wavelength of 200

to 500 nm, a photocurable resin (c) and a photopolymerization initiator (d) are used in combination with the coloring material (a) and the amino resin having a carboxyl group and/or a phenolic hydroxyl group (b).

[0066]

The photocurable resin (c) is a compound having a functional group capable of polymerizing or crosslinking by means of irradiation with ultraviolet rays, visible rays or the like, and typical examples thereof include radically polymerizable compounds and cationically polymerizable compounds. Specific examples thereof include (meth)acrylic compounds, maleimide compounds, vinyl compounds, vinyl ether compounds, epoxide compounds, oxetane compounds, aromatic compounds such as maleic acid ester, fumaric acid ester, crotonic acid ester, N-vinyl pyrrolidone, styrene derivative, and cinnamic acid ester, and N-vinyl imidazole. Among these compounds, compound having a radically polymerizable double bond in the molecule (hereinafter abbreviated to a photocurable compound) is preferable.

[0067]

Specific examples thereof include, but are not limited to, the following compounds.

Examples of the (meth)acrylic compound among the photocurable compounds used in the present invention include trimethylolethane tri(meth)acrylate, trimethylolpropane

tri(meth)acrylate, trimethylolpropane di(meth)acrylate, neopentyl glycol di(meth)acrylate, pentaerythritol tetra(meth)acrylate, pentaerythritol tri(meth)acrylate, dipentaerythritol hexa(meth)acrylate, dipentaerythritol penta(meth)acrylate, hexanediol di(meth)acrylate, trimethylolpropane tri(acryloyloxypropyl) ether, tri(acryloyloxyethyl) isocyanurate, tri(acryloyloxyethyl) cyanurate, and glycerin tri(meth)acrylate;

[0068]

reaction products of (meth)acrylic acid and epoxy resin, such as phenol·novolac type epoxy resin, cresol·novolac type epoxy resin, and bisphenol A type epoxy resin; and reaction products of polyols (e.g. ethylene glycol, polyethylene glycol, polypropylene glycol, polytetramethylene glycol, polyethoxydiol of bisphenol A, polyesterpolyol, polybutadienediol, polycarbonate polyol, etc.), organic polyisocyanates (e.g. tolylene diisocyanate, xylylene diisocyanate, isophorone diisocyanate, hexamethylene diisocyanate, etc.), and hydroxyl group containing (meth)acrylates (e.g. 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 1,4-butanediol mono(meth)acrylate, etc.); and

[0069]

reaction products of (meth)acrylic acid and polyester polyols, which are reaction products of polybasic acid compounds or

anhydrides thereof (for example, maleic acid, succinic acid, adipic acid, isophthalic acid, phthalic acid, terephthalic acid, tetrahydrophthalic acid, hexahydrophthalic acid, and anhydrides thereof) and polyols (for example, ethylene glycol, propylene glycol, 3-methyl-1,5-pentanediol, neopentyl glycol, 1,6-hexanediol, trimethylolpropane, and pentaerythritol).

[0070]

The maleimide compound is preferably a compound wherein a maleimide group is bonded to an aliphatic group, for example, alkyl or alkyl ether maleimide, and specific examples thereof include N-hexyl maleimide or N,N'-4,9-dioxo-1,12-bismaleimidedecane, maleimidecarboxylic acid (poly)alkylene glycol ester such as ethylene glycol bis(maleimide acetate), poly(tetramethylene glycol) bis(maleimide acetate) and tetra(ethylene glycol modified) pentaerythritol tetra(maleimide acetate), carbonate maleimide such as bis(2-maleimideethyl) carbonate, and urethane maleimide such as isophoronebisurethanebis(N-ethylmaleimide).

[0071]

Examples of the vinyl compound include vinyl acetate, vinyl cinnamate, and N-vinylformamide.

[0072]

Examples of the vinyl ether compound include methyl vinyl ether, ethyl vinyl ether, propyl vinyl ether, hydroxymethyl vinyl ether, 2-hydroxyethyl vinyl ether,



chloromethyl vinyl ether, 2-chloroethyl vinyl ether, diethylaminoethyl vinyl ether, cyclobutylmethyl vinyl ether, cyclopentyl vinyl ether, ethylene glycol methyl vinyl ether, diethylene glycol monovinyl ether, and 1,6-hexanediolmethyl vinyl ether.

[0073]

Examples of the styrene derivative include styrene and divinylbenzene.

[0074]

Among these compounds, polyfunctional (meth)acrylates and polyfunctional maleimides, such as trimethylolpropane tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipentaerythritol hexa(meth)acrylate, dipentaerythritol penta(meth)acrylate, N,N'-4,9-dioxa-1,12-bismaleimidedecane, ethylene glycol bis(maleimide acetate), poly(tetramethylene glycol) bis(maleimide acetate), (ethylene glycol modified) pentaerythritol tetra(maleimide acetate), bis(2-maleimideethyl) carbonate, and isophoronebisurethanebis(N-ethylmaleimide) are particularly preferred in view of curing under irradiation with ultraviolet rays, visible rays or the like.

[0075]

These photopolymerizable compounds may be used alone or in combination and the amount thereof is not specifically limited, but is preferred from 25 to 150% by weight based on

the amount of the amino resin in the present invention. When the amount exceeds 150% by weight, the heat resistance of the present invention is less than desired. On the other hand, when the amount is lower than 25% by weight, it becomes difficult to obtain a cured coating layer having the desired physical properties for coating, then it is not preferred.

[0076]

As the photopolymerization initiator, a photopolymerization initiator capable of generating a radical by dissociation upon irradiation with light can be used in the present invention. A conventionally known photopolymerization initiator can be used as such a photopolymerization initiator for the present invention.

Examples of the photopolymerization initiator (d) used in the present invention include benzophenones such as benzophenone, 3,3-dimethyl-4-methoxybenzophenone, 4,4'-bisdimethylaminobenzophenone, 4,4'-bisdiethylaminobenzophenone, 4,4-dichlorobenzophenone, Michler's ketone, and 3,3',4,4'-tetra(t-butylperoxycarbonyl)benzophenone; xanthenes and thioxanthenes, such as xanthone, thioxanthone, 2-methylthioxanthone, 2-isopropylthioxanthone, 2-chlorothioxanthone, 2,4-diethylthioxanthone, 2,4-dimethylthioxanthone, and thioxanthone-4-sulfonic acid;

[0077]

acyloin ethers such as benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzoin-n-butyl ether, benzoin isobutyl ether, and benzoin butyl ether;  $\alpha$ -diketones such as benzyl and diacetyl; sulfides such as tetramethylthiuram monosulfide, tetramethylthiuram disulfide, and p-tolyl disulfide; and benzoic acids such as 4-dimethylaminobenzoic acid, methyl 4-dimethylaminobenzoate, ethyl 4-dimethylaminobenzoate, butyl 4-dimethylaminobenzoate, 4-dimethylaminobenzoic acid-2-ethylhexyl, and 4-dimethylaminobenzoic acid-2-isoamyl;

[0078]

3,3'-carbonyl-bis(7-diethylamino)coumarin, 1-hydroxycyclohexyl phenyl ketone, 2,2-dimethoxy-1,2-diphenylethan-1-one, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-1-one, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one, 2-hydroxy-2-methyl-1-phenylpropan-1-one, 2,4,6-trimethylbenzoyldiphenylphosphine oxide, 1-[4-(2-hydroxyethoxy)phenyl]-2-hydroxy-2-methyl-1-propan-1-one, 1-(4-isopropylphenyl)-2-hydroxy-2-methylpropan-1-one,

[0079]

1-(4-dodecylphenyl)-2-hydroxy-2-methylpropan-1-one, 4-benzoyl-4'-methyldimethyl sulfide, 2,2-diethoxyacetophenone, benzyl dimethyl ketal, benzyl- $\beta$ -methoxyethylacetal, 1-phenyl-1,2-propanedione-2-(o-ethoxycarbonyl)oxime, 2-phenyl-1,2-

butanedione-2-(o-methoxycarbonyl)oxime, 1,3-diphenyl-  
 propanetrione-2-(o-ethoxycarbonyl)oxime, 1-phenyl-3-ethoxy-  
 propanetrione-2-(o-benzoyl)oxime, methyl o-benzoylbenzoate,  
 bis(4-dimethylaminophenyl) ketone,

[0080]

p-dimethylaminoacetophene,  $\alpha,\alpha$ -dichloro-4-phenoxyacetophenone,  
 pentyl-4-dimethylaminobenzoate, 2-(o-chlorophenyl)-4,5-  
 diphenylimidazolyl dimer, 2,4-bis-trichloromethyl-6-[di-  
 (ethoxycarbonylmethyl)amino]phenyl-S-triazine, 2,4-bis-  
 trichloromethyl-6-(4-ethoxy)phenyl-S-triazine, 2,4-bis-  
 trichloromethyl-6-(3-bromo-4-ethoxy)phenyl-S-  
 triazineanthraquinone, 2-t-butylanthraquinone, 2-  
 amylanthraquinone,  $\beta$ -chloroanthraquinone,

[0081]

anthrone, benzanthrone, dibenzsuberone, methylene anthrone,  
 4-azidebenzylacetophenone, 2,6-bis(p-  
 azidebenzylidene)cyclohexane, 2,6-bis(p-azidebenzylidene)-4-  
 methylcyclohexanone, naphthalenesulfonyl chloride,  
 quinolinesulfonyl chloride, n-phenylthioacridone, 4,4-  
 azobisisobutyronitrile, diphenyl disulfide, benzothiazole  
 disulfide, triphenyl phosphine, carbon tetrabromide,  
 tribromophenylsulfone, benzoin peroxide, and combinations of  
 photoreducing pigments such as eosin and methylene blue and  
 reducing agents such as ascorbic acid and triethanolamine.

[0082]

Examples of the trade name of commercially available polymerization initiator include Irgacure #184, Irgacure #149, Irgacure #261, Irgacure #369, Irgacure #500, Irgacure #651, Irgacure #784, Irgacure #819, Irgacure #907, Irgacure #1116, Irgacure #1664, Irgacure #1700, Irgacure #1800, Irgacure #1850, Irgacure #2959, Irgacure #4043 and Darocur #1173 (manufactured by Ciba Specialty Chemicals); Lucirin TPO (manufactured by BASF); KAYACURE-DETX, KAYACURE-MBP, KAYACURE-DMBI, KAYACURE-EPA, and KAYACURE-OA (manufactured by NIPPON KAYAKU CO., LTD.); VICURE #10 and VICURE #55 (manufactured by STAUFFER Co., Ltd.); TRIGONAL P1 (manufactured by AKZO Co., Ltd.); SANDORY 1000 (manufactured by SANDOZ Co., Ltd.); DEAP (manufactured by APJOHN Co., Ltd.); and QUANTACURE-PDO, QUANTACURE-ITX, and QUANTACURE-EPD (manufactured by WARD BLEKINSOP Co., Ltd.).

[0083]

Conventionally known photosensitizers can also be used in combination with the photopolymerization initiator. Examples of the photosensitizer used in the present invention include amines, ureas, sulfur containing compounds, phosphorous containing compounds, chlorine containing compounds, nitriles, and other nitrogen containing compounds. These photosensitizers can be used alone or in combination. The amount is not specifically limited, but is preferred within a range from 0.1 to 30% by weight, and particularly

preferable from 1 to 20% by weight based on the photocurable compound in the composition. When the amount is smaller than 0.1% by weight, the sensitivity tends to lower. On the other hand, if the amount exceeds 30% by weight, precipitation of crystals and deterioration of the physical properties of the coating occurs and, therefore, it is not preferred.

[0084]

The energy-ray curable colored composition for ink jet recording of the present invention can be obtained by mixing the above various components. In this case, proper solvents can be used and the solvent is not specifically limited as long as it does not react with the above respective components, and various solvents which can be used in the preparation of the colored composition containing the coloring material (a) dispersed therein can be used. These solvents can be used alone or in combination. In this case, entire components may be dissolved with the same solvent. Alternatively, the respective components may be optionally dissolved in different solvents to prepare two or more solutions, and these solvents may be mixed to prepare a solution of the energy-ray curable colored composition of the present invention.

[0085]

The viscosity of the energy-ray curable colored composition is preferably adjusted to 50 mPa·s or less, and

particularly preferably 10 mPa·s or less, to facilitate ejecting ink from the ink-jet print head. Therefore, the amount of the solvent is preferably within a range from 1 to 19 parts by weight based on 1 part by weight of the whole solid content.

[0086]

The resulting energy-ray curable colored composition for ink jet recording of the present invention is utilized as one liquid type composition and has superior storage stability and, furthermore, the energy-ray curable colored composition for ink jet recording can be formed by using an aqueous or non-aqueous solvent because an amino resin having a carboxyl group and/or a phenolic hydroxyl group is used. According to the method of the present invention, since a crosslinked structure is formed by the thermocrosslinking reaction of the amino resin in the baking process after formation of the pixels, the resulting color filter has excellent heat resistance and solvent resistance.

[0087]

If necessary, the colored composition used in the present invention may contain other components without departing from the object of the present invention, especially as long as the storage stability, heat resistance, and solvent resistance can be maintained. Examples of such other components include conventionally known coupling agents,

antioxidants, stabilizers, fillers, various leveling agents (e.g. silicon, fluorine, and acrylic leveling agents), polycarboxylic acids and anhydrides thereof used for the purpose of adjusting the solubility to the aqueous solvent, and epoxy compounds used for the purpose of reducing carboxyl groups, remaining in the coating after photocuring, by the thermal reaction.

[0088]

A coupling agent, which is used in the present invention, is a compound which chemically bonds an inorganic material with an organic material, or improves the affinity between them accompanied with the chemical reaction, and thereby enhances the function of the composite material. Typical coupling agents include, for example, silane compounds, titanium compounds or aluminum compounds.

[0089]

Specific examples of the silane coupling agent include  $\gamma$ -(2-aminoethyl)aminopropyltrimethoxysilane and  $\gamma$ -(2-aminoethyl)aminopropylmethyldimethoxysilane;  $\gamma$ -methacryloxypropyltrimethoxysilane,  $\gamma$ -glycidoxypropyltrimethoxysilane and  $\beta$ -(3,4-epoxycyclohexyl)ethyltrimethoxysilane;  $\gamma$ -mercaptopropyltrimethoxysilane; vinyltriacetoxysilane and vinyltrimethoxysilane; trimethoxysilylbenzoic acid;  $\gamma$ -isocyanatopropyltriethoxysilane; and oligomers and polymers



composed of these silane coupling agents.

[0090]

Examples of the titanium coupling agent include tetraisopropoxy titanium, tetra-n-butoxy titanium, tetrakis(2-ethylhexoxy) titanium, tetrastearoxy titanium, diisopropoxy bis(acetylacetonato) titanium, di-n-butoxy bis(triethanolaminato) titanium, dihydroxy bis(lactato) titanium, tetrakis(2-ethylhexanethiolato) titanium, tri-n-butoxytitanium monostearate, isopropyltriisostearoyl titanate, isopropyltridecylbenzenesulfonyl titanate, isopropyltris(dioctylpyrophosphate) titanate, tetraisopropylbis(dioctylphosphite) titanate,

[0091]

tetraoctylbis(ditridecylphosphite) titanate, tetra(2,2-diallyloxymethyl-1-butyl)bis(di-tridecyl)phosphite titanate, bis(dioctylpyrophosphate)oxyacetate titanate, bis(dioctylpyrophosphate)ethylene titanate, isopropyltrioctanoyl titanate, isopropylldimethacrylisostearoyl titanate, isopropylisostearoyldiacryl titanate, isopropyltri(dioctylphosphate) titanate, isopropyltricumylphenyl titanate, isopropyltri(N-aminoethyl aminoethyl) titanate, and dicumylphenyloxycetate titanate, diisostearoylethylene titanate.

[0092]

Examples of the aluminum coupling agent include aluminum isopropylate, monosec-butoxy aluminum diisopropylate, aluminum sec-butyrate, aluminum ethylate, ethylacetoacetate aluminum diisopropylate, aluminum tris(ethylacetoacetate), alkylacetoacetate aluminum diisopropylate, aluminum monoacetylacetate bis(ethylacetoacetate), aluminum tris(acetylacetate), and cyclic aluminum oxide isopropylate.

[0093]

Among these coupling agents, a silane coupling agent having an epoxy group such as  $\gamma$ -glycidoxypropyltrimethoxysilane or  $\beta$ -(3,4-epoxycyclohexyl)ethyltrimethoxysilane is preferred because it imparts remarkably excellent smoothness, adhesion, water resistance, and solvent resistance to various substrates. These coupling agents may be used alone or in combination.

[0094]

The amount of these coupling agents is within a range from 0.1 to 30 parts by weight, and preferably from 0.5 to 20 parts by weight, based on 100 parts by weight of the amino resin (b). When the amount of the coupling agent is 0.1 parts by weight or less, the smoothness, adhesion to the substrate, water resistance, and solvent resistance of the resulting coating layer are insufficient. On the other hand, when the amount exceeds 30 parts by weight, a further improvement in adhesion cannot be expected and the energy-

curability of the resulting coating layer is lowered and, therefore, it is not preferred.

[0095]

Furthermore, epoxy compounds, polycarboxylic acids and acid anhydrides thereof can be added to the energy-ray curable colored composition for ink jet recording of the present invention.

Examples of the epoxy compound include phenol-novolac type epoxy resin, cresol-novolac type epoxy resin, bisphenol A type epoxy resin, bisphenol F type epoxy resin, bisphenol A-novolac type epoxy resin, alicyclic epoxy resin, various glycols or alkylene oxide-modified epoxy resin, and acrylic resin containing glycidyl group or alicyclic epoxy group. These epoxy compounds can be used alone or in combination.

[0096]

Typical examples of the polycarboxylic acids and acid anhydrides thereof include aliphatic polyvalent carboxylic acids such as succinic acid, glutaric acid, adipic acid, butane tetracarboxylic acid, maleic acid, and itaconic acid; alicyclic polyvalent carboxylic acids such as hexahydrophthalic acid, 1,2-cyclohexane carboxylic acid, 1,2,4-cyclohexane tricarboxylic acid, and cyclopentanetetracarboxylic acid, and phthalic acid, isophthalic acid, terephthalic acid, trimellitic acid, pyromellitic acid, 1,4,5,8-naphthalene tetracarboxylic acid,

benzophenone tetracarboxylic acid;

[0097]

fatty acid dicarboxylic acid anhydrides such as phthalic anhydride, itaconic anhydride, succinic anhydride, citraconic anhydride, dodecenylsuccinic anhydride, tricarbarlylic anhydride, maleic anhydride, hexahydrophthalic anhydride, methyltetrahydrophthalic anhydride, and himic anhydride; aliphatic polyvalent carboxylic acid dihydrides such as 1,2,3,4-butanetetracarboxylic dianhydride; pyromellitic anhydride, trimellitic anhydride, or benzophenonetetracarboxylic anhydride; and ester group-containing acid anhydrides such as ethylene glycol bistrimellitate and glycerin tristrimellitate.

[0098]

Furthermore, commercially available epoxy resin curing agents made of colorless carboxylic anhydride can also be used preferably. Specific examples thereof include Adeka Hardner EH-700 (trade name, manufactured by Asahi Denka Kogyo corpo.), RIKACID-MH and RIKACID MH-700 (manufactured by New Japan Chemical Co., Ltd.), and EPIKINI 126, EPIKINI YH-306 and EPIKINI DX-126 (manufactured by YUKA SHELL EPOXY Co., Ltd.).

[0099]

Furthermore, as the polyvalent carboxylic acid and anhydride thereof, a resin having two or more carboxyl groups

in a molecule or an anhydride thereof can be preferably used. Specific examples thereof include urethane resin, acrylic resin, polyester resin, lactone-modified polyester resin, polyesteramide resin, alkyd resin, polyether resin, modified polyether resin, polythioether resin, polycarbonate resin, polyacetal resin, polyolefin resin, epoxy-modified resin, silicone resin, and fluorine resin, each having a carboxyl group, or acid anhydrides thereof.

The polyvalent carboxylic acids and polyvalent carboxylic anhydrides described above can be used alone or in combination.

[0100]

The film with desired patterns can be obtained by forming a color filter pattern with the energy-ray curable colored composition for ink jet recording of the present invention on the surface of a substrate by the ink-jet printing method, and then curing the color filter pattern by means of irradiation with energy ray, namely by irradiation with light having a wavelength of 200 to 500 nm and/or by heat treatment.

[0101]

A solution containing the energy-ray curable colored composition for ink jet recording of the present invention is applied to the surface of the substrate by a conventionally known ink jet technique. Examples of the ink-jet printing

method used in the present invention include the bubble-jet method using a converter which converts electricity to heat as an energy generating element, and a piezo-jet method using a piezo-electric element.

[0102]

To form a colored pattern, the energy-ray curable colored composition for ink jet recording used in the present invention is first ejected through the ink ejecting head according to the ink-jet printing method on a substrate provided with a black matrix, thereby to form a predetermined colored pattern. The black matrix can be formed on the substrate by a known method such as a method of forming a metal thin film by a sputtering or vacuum deposition method, followed by patterning with a photolithography method, a method of patterning by a photolithography process using a black colored resin composition, or an ink-jet printing method. According to properties of the colored composition, the black matrix can be subjected to a treatment of hydrophilicity, a treatment of hydrophobicity, or a treatment of oil repellency. It is effective and possible to subject the substrate to a surface treatment using an auxiliary adhesive such as a coupling agent as a means for enhancing adhesion between the substrate and the pixel patterns. The substrate can be provided with an ink-jet ink receiving layer.

[0103]

For example, the color filter can be formed by the following method. The energy-ray curable colored composition for ink jet recording used in the present invention is first ejected through the ink ejecting head according to the ink-jet printing method on a substrate provided with a black matrix by, thereby to form a predetermined colored pattern, and then the inks of the patterns are cured by irradiation with light and/or heat treatment. If necessary, a protective film is formed and, furthermore, transparent conductive electrodes such as ITO are optionally formed after the after-baking process. The method of forming a color filter is not limited to the method described above.

[0104]

Examples of the heat source used in thermosetting of the energy-ray curable colored composition for ink jet recording include conventionally known heat sources such as hot plates, electric ovens, and infrared ray heating furnaces. The heating temperature is preferably within a range from 150 to 300°C. When the temperature is lower than 150°C, the film strength, the solvent resistance, and the alkali resistance are poor because of insufficient thermosetting. On the other hand, when the temperature exceeds 300°C, excess volume shrinkage occurs and thus problems in adhesion to the substrate and accuracy are likely to occur, and this is not preferred.

[0105]

A light source used for photocuring of the energy-ray curable colored composition for ink jet recording is preferably a light source capable of emitting ultraviolet rays to visible rays, and a particularly preferable light source is a light source for emitting light having a wavelength of 200 to 500 nm. From an economic viewpoint, ultraviolet rays are particularly preferred. Examples of a source capable of emitting ultraviolet rays or visible rays include low-pressure mercury lamps, high-pressure mercury lamps, extra-high-pressure mercury lamps, metal halide lamps, chemical lamps, black light lamps, mercury-xenon lamps, excimer lamps, short arc lamps, helium-cadmium lasers, argon lasers, and THG or FHG lasers using Nd-YAG lasers. The photocuring conditions vary depending on the kind of the light source and the kind and amount of the photopolymerization initiator, and therefore, it cannot be specifically defined. However, from the viewpoint of the productivity, the dose is preferably within a range from 100 to 3,000 J/cm<sup>2</sup>. When both photopolymerization and thermosetting processes are applied to produce a color filter, the thermosetting conditions described above are applied.

[0106]

The energy-ray curable colored composition for ink jet recording of the present invention can be preferably used in



the color filter such as color liquid crystal displays, color scanners, and solid image pick-up elements.

The color filter is formed by arranging coloring materials on each pixel to selectively transmit three primary colors of light (e.g., red, green, and blue) or to selectively reflect three primary colors (e.g., cyan, magenta, and yellow), on a transparent substrate provided with a shielding film called as a black matrix.

[0107]

According to the energy-ray curable colored composition for ink jet recording of the present invention, it is made possible to form colored pixels of three primary colors of light (e.g., red, green, and blue) or three primary colors of color (e.g., cyan, magenta, and yellow) as well as black pixel used for shielding light, by a simple process using the above method such that plural different colors are simultaneously formed on a substrate by means of an ink-jet printing method, followed by exposure and/or baking. By using the energy-ray curable colored composition for ink jet recording of the present invention, a color filter having excellent heat resistance, solvent resistance and chemical resistance can be produced.

[0108]

#### [EXAMPLES]

The present invention will be described in detail by

way of the following Examples, but the present invention is not limited by the Examples. In the following Examples, parts and percentages are by weight unless otherwise indicated. Performance tests of the resulting coatings were carried out by the following procedures.

[0109]

<Performance test and evaluation criteria>

<<Storage stability>>

The viscosity was measured after an energy-ray curable colored composition for ink jet recording was stored at 40°C for 24 hours. Test samples where the change in viscosity relative to the initial viscosity was smaller than 10% were rated "good (O)", while test samples where the change in viscosity relative to an initial viscosity was larger than 10% were rated "poor (X)". The viscosity was measured by using an E type viscometer manufactured by TOKIMEC INC.

[0110]

<<Curing conditions>>

Photopolymerization conditions: A pattern was formed by an ink-jet printing method, dried at 110°C for 10 minutes, and then cured by exposing to light from a high-pressure mercury lamp at a dose of 1000 J/m<sup>2</sup>.

Thermosetting conditions: A pattern was formed by an ink-jet printing method, dried at 110°C for 10 minutes, and then cured in an oven at 200°C for 30 minutes.

After-baking: After the photopolymerization or the thermosetting, the after-baking was carried out at 230°C for 15 minutes.

[0111]

<<Evaluation of physical properties of coating layer>>

Heat resistance 1: The coating layer obtained by coating on the glass substrate using an ink-jet printing method and subsequently curing was heated at 280°C for 30 minutes and the heat resistance 1 was evaluated by the change in transparency (Y value) in the color hue before and after heating. Test samples where the difference  $\Delta Y$ , which is a rate of change, is smaller than 0.5 were rated "good (○)", while test samples where the difference  $\Delta Y$  is larger than 0.5 were rated "poor (×)". The chromaticity was measured by a microscopic spectrophotometer OSP-SP200 manufactured by OLYMPUS OPTICAL CO., LTD.

[0112]

Heat resistance 2: The coating layer obtained by coating on the glass substrate using an ink-jet printing method and subsequently curing was heated at 280°C for 30 minutes and the heat resistance 2 was evaluated by the change in maximum light transmittance before and after heating. Test samples where the difference in maximum light transmittance was smaller than 5% were rated "good (○)", while test samples where the difference in maximum light

transmittance was larger than 5% were rated "poor (×)".

[0113]

Chemical resistance 1: The coating layer obtained by application to a glass substrate using an ink-jet printing method and subsequently curing was dipped in N-methyl-2-pyrrolidone at 23°C for 30 minutes and the boundary surface of the dipped portion was observed. Test samples where the boundary line could not be visually confirmed were rated "good (○)", while test samples where the boundary line could be visually confirmed were rated "poor (×)".

[0114]

Chemical resistance 2: The coating layer obtained by application to a glass substrate using an ink-jet printing method and subsequently curing was rubbed with acetone at 25°C under a load of 100 g using a rubbing tester [manufactured by Taihei Rika Kogyo Co., Ltd.] and the number of rubs required to expose the glass substrate as a base was determined. Test samples where the number of rubs was less than 25 were rated "poor (×)", test samples where the number of rubs was 25 or more and less than 100 were rated "good (○)", and test samples where the number of rubs was more than 100 were rated "excellent (◎)".

[0115]

Preparation Example 1 [preparation of amino resin having carboxyl group]

In a four-necked flask equipped with a thermometer, a reflux condenser, and a stirrer, 131.7 parts of 2-(4,6-diamino-1,3,5-triazin-2-yl)benzoic acid containing 12.3 parts of water, 202.8 parts of an aqueous 37% formaldehyde solution, and 222.3 parts of n-butanol were charged, and then the four-necked flask was dipped in an oil bath preheated to 115°C with stirring. After 15 minutes, the mixture became a uniform solution and refluxing was initiated. After the reaction was continued for two hours, water and excess formaldehyde were distilled off under a reduced pressure of  $5.33 \times 10^4$  Pa over three hours.

[0116]

After water and n-butanol were distilled off, propylene glycol monomethyl ether acetate (hereinafter abbreviated to PGMAc) was added and the mixture was cooled. PGMAc was further added to adjust the nonvolatile content (% by weight of residual resin after drying at 107.5°C for one hour) to be 40.0%. As a result, an amino resin (A-1) having a carboxyl group, wherein the acid value (the number of milligrams of potassium hydroxide required to neutralize an acid content in 1 g of a sample according to a defined method) of the resin solid content was 94.6 mg KOH/g was obtained. The number-average molecular weight  $M_n$  calculated in terms of polystyrene was 2150 and the molecular weight distribution  $M_w/M_n$  was 5.12.

[0117]

Preparation Example 2 [preparation of amino resin having carboxyl group]

In a four-necked flask equipped with a thermometer, a reflux condenser, and a stirrer, 37.4 parts benzoguanamine, 118.4 parts of an aqueous 50% glyoxylic acid solution, and 88.8 parts of n-butanol were charged, and then the four-necked flask was dipped in an oil bath preheated to 115°C with stirring. After 15 minutes, the mixture became a uniform solution and refluxing was initiated. After the reaction was continued for one hour, water and excess formaldehyde was distilled off under a reduced pressure of  $5.33 \times 10^4$  Pa over four hours. Subsequently, water and n-butanol were distilled off, PGMAc was added and the mixture was cooled. The PGMAc was further added to adjust the nonvolatile content to be 40.0%. As a result, an amino resin (A-2) having a carboxyl group, wherein the acid value of the resin solid content was 136 mg KOH/g was obtained. The number-average molecular weight  $M_n$  calculated in terms of polystyrene was 1624 and the molecular weight distribution  $M_w/M_n$  was 1.28.

[0118]

Preparation Example 3 [preparation of amino resin having phenolic hydroxyl group]

In a four-necked flask equipped with a thermometer, a

reflux condenser, and a stirrer, 18.7 parts of benzoguanamine, 48.8 parts of p-hydroxybenzaldehyde, and 88.8 parts of n-butanol were charged, and then the four-necked flask was dipped in an oil bath preheated to 125°C with stirring. After 20 minutes, the mixture became a uniform solution. The reaction was continued at the same temperature for 24 hours. After the completion of the reaction, n-butanol was distilled off under a reduced pressure of  $5.33 \times 10^4$  Pa and the resulting solid was washed with a mixed solution of n-hexane and ethyl acetate in a mixing ratio of 2:1 to remove excess p-hydroxybenzaldehyde. PGMAc was added and the mixture was cooled. PGMAc was further added to adjust the nonvolatile content to be 40.0%. As a result, an amino resin (A-3) having a phenolic hydroxyl group, wherein the acid value of the resin solid content was 85.2 mg KOH/g was obtained. The number-average molecular weight  $M_n$  calculated in terms of polystyrene was 4000 and the molecular weight distribution  $M_w/M_n$  was 3.26.

[0119]

Preparation Example 4 [preparation of acrylic resin having carboxyl group]

In a four-necked flask equipped with a thermometer, a reflux condenser, a stirrer, and a nitrogen gas introducing inlet, 425.0 parts of PGMAc was charged and, after heating to 90°C with stirring, a mixture of 42.8 parts of methacrylic

acid (hereinafter abbreviated to MAA), 286.1 parts of benzyl methacrylate (hereinafter abbreviated to BzMA), 96.0 parts of PGMAc, and 16.5 parts of t-butylperoxy-2-ethyl hexanoate (hereinafter abbreviated to P-O) was added dropwise over one hour. After the completion of the dropwise addition, the mixture was maintained at 90°C for two hours and 1.7 parts of "P-O" was added. Furthermore, the reaction was carried out at the same temperature for seven hours to obtain a solution containing an acrylic resin (A-4) having a carboxyl group, wherein the acid value of the resin solid content was 84.0 mg KOH/g. The nonvolatile content of the resulting resin solution was 39.7%, the number-average molecular weight  $M_n$  calculated in terms of polystyrene was 9500, and the molecular weight distribution  $M_w/M_n$  was 2.07.

[0120]

#### Example 1

Using a high-speed dispersing machine "TSG-6H" (manufactured by Igarashi Kikai Seizo) charged with zirconia beads having 0.5 mm  $\phi$ , a dispersion comprising 25.0 parts of an amino resin solution (A-1) having a carboxyl group prepared in Preparation Example 1, 8.0 parts of Pigment Red 254, 2.5 parts of AJISPER PB814 as a dispersant, and 64.5 parts of PGMAc was dispersed at 2000  $m^{-1}$  for eight hours to obtain a red pigment dispersion. Then, 7.0 parts of dipentaerythritol hexaacrylate (hereinafter abbreviated to



DPHA) and 0.3 parts of Irgacure #369 were added to 100 parts of the red pigment dispersion and, after mixing them, the mixture was filtered through a filter having a pore diameter of 1.0  $\mu\text{m}$  to obtain a photocurable colored composition for ink jet recording (R-1). 25 g of the resulting photocurable colored composition for ink jet recording (R-1) was transferred to a glass container and stored at 40°C for 24 hours after sealing. The storage stability was evaluated according to the procedures of the performance tests. As a result, the storage stability was found to be good.

[0121]

Pixel patterns were formed using the photocurable colored composition for ink jet recording (R-1) by a piezo ink-jet type print head, and then pre-baked at 110°C for 10 minutes to form red coating patterns. The resulting coating patterns were exposed to light from a high-pressure mercury lamp at a dose of 1000 J/m<sup>2</sup>. The resulting coating patterns were thermoset at 230°C for 15 minutes and then evaluated according to items of the performance test. The evaluation results are shown in Table 1. As a result, these red pixel patterns for a color filter were found to have superior heat resistance and superior chemical resistance. The absorption spectra and thin-film X-ray diffractions of the coating layer after the heat resistance test were measured. No changes in crystal form or increases in the crystal size of the red

pigment were observed.

[0122]

#### Example 2

A photocurable colored composition for ink jet recording (R-2) was obtained in the same manner as in Example 1, except that the amino resin (A-1) used in Example 1 was replaced by an amino resin (A-2) obtained in Preparation Example 2. 25 g of the resulting photocurable colored composition for ink jet recording (R-2) was transferred to a glass container and stored at 40°C for 24 hours after sealing, and the storage stability was evaluated. As a result, the storage stability was found to be good.

[0123]

Then, pixel patterns were formed on a glass substrate using the photocurable colored composition for ink jet recording (R-2) in the same manner as in Example 1. In the same manner as in Example 1, the resulting coating patterns were exposed and after-baked, and then evaluated according to items of the performance test. The evaluation results are shown in Table 1. As a result, these red pixel patterns for a color filter were found to have superior heat resistance and superior chemical resistance. The absorption spectra and thin-film X-ray diffractions of the coating layer after the heat resistance test were measured. No changes in crystal form or increases in the crystal size of the red pigment were

observed.

[0124]

### Example 3

A photocurable colored composition for ink jet recording (R-3) was obtained in the same manner as in Example 1, except that the amino resin (A-1) used in Example 1 was replaced by an amino resin (A-3) obtained in Preparation Example 3. 25 g of the resulting photocurable colored composition for ink jet recording (R-3) was transferred to a glass container and stored at 40°C for 24 hours after sealing, and the storage stability was evaluated. As a result, the storage stability was found to be good.

[0125]

Then, pixel patterns were formed on a glass substrate using the photocurable colored composition for ink jet recording (R-3) in the same manner as in Example 1. In the same manner as in Example 1, the resulting coating patterns were exposed and thermoset, and then evaluated according to items of the performance test. The evaluation results are shown in Table 1. As a result, these red pixel patterns for a color filter were found to have superior heat resistance and superior chemical resistance. The absorption spectra and thin-film X-ray diffractions of the red pixel patterns after the heat resistance test were measured. No changes in crystal form or increases in the crystal size of the red

pigment were observed.

[0126]

#### Example 4

A photocurable colored composition for ink jet recording (R-4) was obtained in the same manner as in Example 1, except that 25 parts of the amino resin (A-1) obtained in Preparation Example 1 was replaced by a mixture of 12.5 parts of the amino resin (A-1) obtained in Preparation Example 1 and 12.5 parts of the acrylic resin (A-4) obtained in Preparation Example 4. In the same manner as in Example 1, the storage stability and various physical properties of the coating layer were evaluated. The evaluation results are shown in Table 1.

As a result, the resulting composition was found to have good storage stability, and the red pixel patterns for a color filter were found to have superior heat resistance and superior chemical resistance. The absorption spectra and thin-film X-ray diffractions of the coating layer after the heat resistance test were measured. No changes in crystal form or increases in crystal size of the red pigment were observed.

[0127]

#### Example 5

A photocurable colored composition for ink jet recording (R-5) was obtained in the same manner as in Example

1, except that the photocurable resin DPHA used in Example 1 was replaced by pentaerythritol triacrylate (hereinafter abbreviated as PETA). In the same manner as in Example 1, the storage stability and various physical properties of the coating layer were evaluated. The evaluation results are shown in Table 1.

As a result, the resulting composition was found to have good storage stability, and the red pixel patterns for a color filter were found to have superior heat resistance and superior chemical resistance. The absorption spectra and thin-film X-ray diffractions of the coating layer after the heat resistance test were measured. No changes in crystal form or increases in crystal size of the red pigment were observed.

[0128]

#### Example 6

A photocurable colored composition for ink jet recording(R-6) was obtained in the same manner as in Example 1, except that the photocurable resin DPHA used in Example 1 was replaced by poly(tetramethylene glycol) bis(maleimide acetate) [average molecular weight of poly(tetramethylene glycol): 250] (hereinafter abbreviated to MIA250). In the same manner as in Example 1, the storage stability and various physical properties of the coating layer were evaluated. The evaluation results are shown in Table 1.

As a result, the resulting composition was found to have good storage stability, and the red pixel patterns for a color filter were found to have superior heat resistance and superior chemical resistance. The absorption spectra and thin-film X-ray diffractions of the coating layer after the heat resistance test were measured. No changes in crystal form or increases in crystal size of the red pigment were observed.

[0129]

#### Comparative Example 1

A photocurable colored composition for ink jet recording (R-7) for comparison was obtained in the same manner as in Example 1, except that the amino resin (A-1) used in Example 1 was replaced by an acrylic resin (A-4) obtained in Preparation Example 4. In the same manner as in Example 1, the storage stability of the colored composition (R-7) and various physical properties of the coating layer were evaluated. The evaluation results are shown in Table 1.

As a result, the resulting composition was found to have good storage stability, but the resulting coating layer is inferior in heat resistance and chemical resistance. The absorption spectra and thin-film X-ray diffractions of the coating layer after the heat resistance test were measured. An increase in the crystal size of the red pigment was observed.

It is apparent from comparison between a color filter of Comparative Example 1 and those of Examples 1 to 6 that, when using only an acrylic resin as the binder resin, the pixel patterns of the resulting red pixel patterns are inferior in heat resistance and chemical resistance.

[0130]

[Table 1]

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Comparative Example 1
Composition of photocurable resin							
Amino resin solution	A-1 25.0	A-2 25.0	A-3 25.0	A-1 12.5	A-1 25.0	A-1 25.0	R-7
Acrylic resin solution	-	-	-	A-4 12.5	-	-	A-4 25.0
Red pigment dispersion	100	100	100	100	100	100	100
Photocurable resin	DPHA 7.0	DPHA 7.0	DPHA 7.0	DPHA 7.0	PETA 7.0	MIA250 7.0	DPHA 7.0
Irg-#369	0.3	0.3	0.3	0.3	0.3	0.3	0.3
Performance of coating patterns							
Storage stability	○	○	○	○	○	○	○
Heat resistance 1	⊙	○	○	⊙	⊙	⊙	×
Heat resistance 2	⊙	○	○	⊙	⊙	⊙	×
Appearance of coating patterns after heat resistance test	good	good	good	good	good	good	slightly uneven surface
Chemical resistance 1	○	○	○	○	○	○	○
Chemical resistance 2	○	○	○	○	○	○	×



[0131]

All numbers in the table indicate parts by weight.

DPHA: dipentaerythritol hexaacrylate

PETA: pentaerythritol triacrylate

MIA250: poly(tetramethylene glycol) bis(maleimide acetate)

[average molecular weight of poly(tetramethylene glycol):

250]

Irg #369: Irgacure #369

[0132]

#### Example 7

Using a high-speed dispersing machine "TSG-6H" (manufactured by Igarashi Kikai Seizo) charged with zirconia beads having 0.5 mm  $\varnothing$ , a dispersion consisting of 25.0 parts of a solution containing an amino resin (A-1) having a carboxyl group prepared in Preparation Example 1, 8.0 parts of Pigment Blue 15:6, and 2.5 parts of "DISPERBYK 163" as a dispersant, and 64.5 parts of PGMAc was dispersed at 2000  $\text{m}^{-1}$  for eight hours and the mixture was filtered through a filter having a pore diameter of 1.0  $\mu\text{m}$  to obtain a thermosetting colored composition for ink jet recording (B-1). 25 g of the resulting thermosetting colored composition for ink jet recording (B-1) was transferred to a glass container and stored at 40°C for 24 hours after sealing. The storage stability was evaluated. As a result, the storage stability was found to be good.

[0133]

The thermosetting colored composition for ink jet recording (B-1) was coated on a glass substrate by a piezo ink-jet type print head, and then pre-baked at 110°C for 10 minutes to form blue coating patterns. The resulting coating patterns were cured in an oven at 200°C for 30 minutes. The resulting coating layer patterns were after-baked at 230°C for 15 minutes. The coating layer patterns were evaluated in accordance with each of the performance tests.

As a result, these blue pixel patterns for a color filter were found to have superior (◎) heat resistance 1, superior (◎) heat resistance 2, good appearance of coating patterns after heat resistance test, good (○) chemical resistance 1, good (○) chemical resistance 2, superior heat resistance and superior chemical resistance. The absorption spectra and thin-film X-ray diffractions of the coating layer after the heat resistance test were measured. Changes in crystal form and increases in crystal size of the blue pigment were not observed.

[0134]

#### Comparative Example 2

A thermosetting colored composition (B-2) for comparison was obtained in the same manner as in Example 7, except that the 25.0 parts of the amino resin solution (A-1) having a carboxyl group prepared in Preparation Example 1 was

replaced by 25.0 parts by weight of a malamine resin [SUPER BECKAMINE J-820-60 (n-butanol/xylene solution), manufactured by DAINIPPON INK & CHEMICALS, Inc.]. In Comparative Example 2, the dispersibility of the blue pigment was poor and the ejecting properties were poor when ejected onto the glass substrate using a piezo ink-jet type print head, thus causing clogging of the head. Therefore, evaluations according to items of the performance test were not carried out.

As is apparent from the above results, the thermosetting colored composition of Comparative Example 2 is inferior in performance to the thermosetting colored composition using the amino resin solution having a carboxyl group of Example 7.

[0135]

[Effects of the Invention]

By using, as a binder resin, an amino resin having a carboxyl group and/or a phenolic hydroxyl group, and a color filter, it is made possible to provide an energy-ray curable colored composition for ink jet recording suited for practical use, which is superior in storage stability and can easily form colored patterns by means of an ink-jet printing method and form a coating layer having excellent heat resistance and solvent resistance or chemical resistance, especially heat resistance, and a color filter using the same.

[Document Type] Abstract

[Abstract]

[Object] To provide an energy-ray curable colored composition for ink jet recording suited for practical use, which is superior in storage stability and can easily form colored patterns by means of an ink-jet printing method and form a coating layer having excellent heat resistance and solvent resistance or chemical resistance, and a color filter using the same.

[Means for Solving the Problems] An energy-ray curable colored composition for ink jet recording, comprising (a) a coloring material and (b) an amino resin having a carboxyl group and/or a phenolic hydroxyl group, and a color filter.

[Elected Drawing] None